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Letter

Low and small resistance hole-injection barrier for NPB realized by wide-gap p-type degenerate semiconductor, LaCuOSe:Mg

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ABSTRACT

LaCuOSe:Mg is a wide-gap p-type semiconductor with a high conductivity and a large work function. Potential of LaCuOSe:Mg as a transparent hole-injection electrode of organic light-emitting diodes (OLEDs) was examined by employing *N*,*N*′-diphenyl-*N*,*N*′-bis (1,1′-biphenyl)-4,4′-diamine (NPB) for a hole transport layer. Photoemission spectroscopy revealed that an oxygen plasma treated surface of LaCuOSe:Mg formed a hole-injection barrier as low as 0.3 eV, which is approximately a half of a conventional ITO/NPB interface. Hole-only devices composed of a LaCuOSe:Mg/NPB/Al structure showed a low threshold voltage ~0.2 V and high-density current drivability of 250 mA cm^{-2} at 2 V, which is larger by two orders of magnitude than that of ITO/NPB/Al devices. These results demonstrate that LaCuOSe:Mg has great potential as an efficient transparent anode for OLEDs and other organic electronic devices.

One of the critical issues of organic light-emitting diodes (OLEDs) is to reduce operation voltages, which are mainly controlled by carrier injections through hetero-interfaces with large band discontinuities (carrier injection barriers). In addition, an anode or a cathode in an OLED must be transparent to release light to the surrounding environment. In conventional structures, Sn-doped In_2O_3 (ITO) is used as a transparent anode because ITO has both a high conductivity and high transparency in the visible region. The rather large work functions of ITO (4.4–4.7 eV for metallic ITO [1]) are another advantage for the anode because a large work function material would reduce the hole-injection barrier (E_{HIB}) for an organic hole transport material, which typically has a large ionization potential that corresponds to the energy level of the highest occupied molecular orbital (HOMO) that forms the hole transport orbital. However, the ionization potentials of common hole transport materials are 4.7–6.0 eV, which are larger than the work functions of metallic ITO. Therefore, the ITO surface is subjected to oxidation treatments such as UV-O_3 and oxygen plasma treatments to increase the work functions to 4.8–5.4 eV, [2–4] which consequently decrease the E_{HIB} value to 0.6 eV. [3] However, oxidation treatments decrease the carrier concentrations in the surface region of the ITO and increase their contact resistances because the majority carriers in ITO are electrons. Hence, we believe that p-type transparent materials

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[5,6] are better suited for improving the hole-injection properties because we anticipate that a higher work function will be compatible with the smaller resistance in p-type materials. From this view, Mg-doped LaCuOSe (LaCuOSe:Mg) is an attractive candidate because it is a transparent p-type semiconductor that shows a degenerate conduction with conductivities as high as 910 S cm^{-1} [7] and large work functions of ~5 eV.

Herein we report that a low E_{HIB} of 0.3 eV is formed at LaCuOSe:Mg/*N*,*N*′-diphenyl-*N*,*N*′-bis(1,1′-biphenyl)-4,4′-diamine (NPB) interfaces. The E_{HIB} values were measured by ultraviolet photoemission spectroscopy (UPS), and the interface electrical properties were characterized using hole-only devices composed of a LaCuOSe:Mg/NPB/Al structure. These observations substantiated that employing LaCuOSe:Mg as an anode improves the electrical characteristics; i.e., a low threshold voltage of <0.2 V and a high current drivability of 250 mA cm^{-2} at 2 V were obtained.

Epitaxial films of LaCuOSe:Mg fabricated on (001) MgO single crystals were employed in this study to determine the fundamental interface properties with a well-defined structure. The epitaxial films of LaCuOSe:Mg were prepared on single-crystalline MgO(001) substrates by a reactive solid-phase epitaxy (R-SPE) process [8–10]. In this process, a thin Cu layer (5 nm in thickness) was initially deposited on an MgO(001) substrate under a high vacuum of 10^{-5} Pa at 400 °C by pulsed laser deposition (PLD). An amorphous LaCuOSe:Mg layer was then deposited on the thin Cu layer at room temperature sequentially in the same PLD chamber. A sintered ceramic disk of LaCuOSe:Mg was used as the PLD target. The obtained films were annealed at 1000 °C with a small amount of LaCuOSe powder in evacuated silica glass ampoules. The surfaces of the obtained films were polished by chemical–mechanical polishing (CMP), which produced an atomically flat, terrace-and-step surface with root-mean-square roughnesses (R_{rms}) of 0.6–1.5 nm. The film thickness was fixed between 30 and 50 nm because it was confirmed that LaCuOSe:Mg exhibits the largest hole concentration and the highest conductivity for thicknesses less than 50 nm [7]. It should be noted that the small thickness of the LaCuOSe:Mg layer causes a somewhat high series resistance for hole-only devices, as will be discussed later. However, the series resistance is small enough to obtain a large injection current, which demonstrates the improved injection properties of the LaCuOSe:Mg/NPB interface. The electrical conductivity, hole concentration, and Hall mobility of the LaCuOSe:Mg films used in this study were >500 S cm^{-1}, >1 × 10^{21} cm^{-3}, and ~3 cm^2 V^{-1} s^{-1}, respectively, at room temperature. Details of the optical and electrical properties are reported in Ref. [7].

The LaCuOSe:Mg films were then transferred to a multichamber system equipped with two preparation chambers, two organic/metal evaporation chambers, an X-ray photoemission spectroscopy (XPS)/ultraviolet photoemission spectroscopy (UPS) chamber, and an electrical/light-emission measurement chamber connected in an ultra-high vacuum at 10^{-6} Pa. Residual atmospheric contaminants and polishing residues on the surfaces of the LaCuOSe:Mg films were removed in the preparation chamber by an oxygen plasma treatment (radio frequency (RF) plasma in a pure O_2 gas at 6.0 × 10^{-1} Pa for 30 s with an RF power of 50 W). Observations of C 1s peak intensities by XPS confirmed that carbon contaminants were removed by the oxygen plasma treatment. XPS measurements also revealed that the oxygen plasma treatment oxidized the LaCuOSe:Mg surface, and the valence state of Cu^+ at the surface of LaCuOSe:Mg changed to Cu^{2+}. The LaCuOSe:Mg films maintained the same high conductivity after the treatment.

Sublimation-purified NPB (Lumtec, Taiwan) was deposited by thermal vacuum evaporation at deposition rates of 0.07–0.15 nm s^{-1}, a pressure of 2 × 10^{-6} Pa, and a substrate temperature of room temperature. The thickness of the NPB film was monitored with a pre-calibrated quartz-oscillator thickness meter. UPS measurements under an ultra-high vacuum (5 × 10^{-8} Pa) and thin layer depositions of NPB were alternately repeated by transferring the sample between the UPS chamber and the deposition chamber in vacuum to collect UPS spectra as a function of NPB thickness.

Single-crystalline (sc-) ITO films prepared by PLD [11] and commercially-available polycrystalline (pc-) ITO films (Asahi Glass Co., Ltd.) were examined for comparison. Before the deposition of NPB, the sc- and pc-ITO films were treated by the oxygen plasma (50 W, 6.0 × 10^{-1} Pa with durations of 30 s for sc-ITO and 3 min for pc-ITO), and annealed in vacuum in the other preparation chamber (250 °C, ~5 × 10^{-6} Pa, 5 min) to obtain conductive ITO films with large work functions (~5 eV). An Al/NPB interface was also examined by *in situ* UPS measurements.

Fig. 1 shows the UPS spectra of the LaCuOSe:Mg/NPB interfaces as a function of NPB thickness (*t*). The work

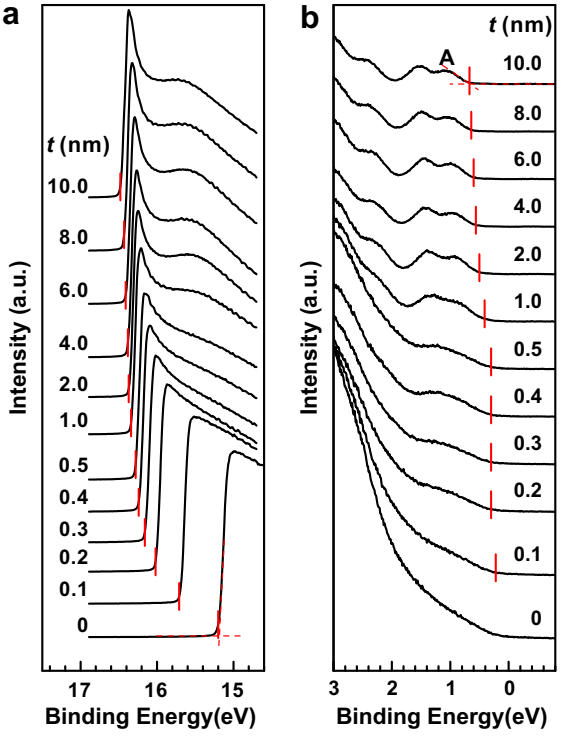

Fig. 1. Variation of UPS spectra of LaCuOSe:Mg/NPB interface with NPB thickness. (a) Cut-off and (b) valence region.